ACS central science

# A Robust Damage-Reporting Strategy for Polymeric Materials Enabled by Aggregation-Induced Emission

Maxwell J. Robb,[†,‡,§] Wenle Li,[†,§,‖] Ryan C. R. Gergely,[†,⊥] Christopher C. Matthews,[†,⊥] Scott R. White,[†,#] Nancy R. Sottos,*[,†,‖] and Jeffrey S. Moore*[,†,‡]

[†]The Beckman Institute for Advanced Science and Technology, [‡]Department of Chemistry, [‖]Department of Materials Science and Engineering, [⊥]Department of Mechanical Science and Engineering, and [#]Department of Aerospace Engineering, University of Illinois at Urbana—Champaign, Urbana, Illinois 61801, United States

S *Supporting Information*

ABSTRACT: Microscopic damage inevitably leads to failure in polymers and composite materials, but it is difficult to detect without the aid of specialized equipment. The ability to enhance the detection of small-scale damage prior to catastrophic material failure is important for improving the safety and reliability of critical engineering components, while simultaneously reducing life cycle costs associated with regular maintenance and inspection. Here, we demonstrate a simple, robust, and sensitive fluorescence-based approach for autonomous detection of damage in polymeric materials and composites enabled by aggregation-induced emission (AIE). This simple, yet powerful system relies on a single active component, and the general mechanism delivers outstanding performance in a wide variety of materials with diverse chemical and mechanical properties.
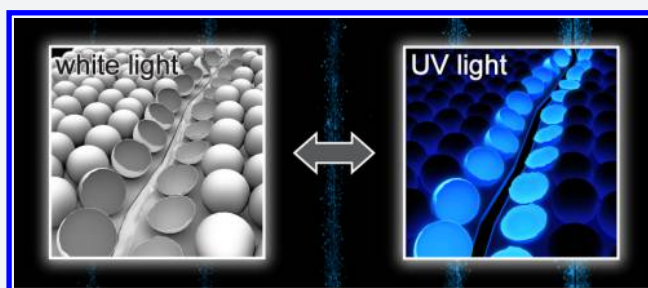
Small (micrometer) scale damage in polymeric materials is often difficult to detect, yet it compromises mechanical integrity and inevitably leads to failure. Strategies that enhance detection of damage are therefore important for improving safety and increasing reliability, while also reducing life cycle costs associated with regular maintenance and inspection.[1,2] Moreover, systems that respond autonomously to self-report damage are appealing because no human intervention is required.

The development of self-reporting materials enables autonomous damage detection for improved safety and reliability of critical engineering components. For example, incorporation of mechanically sensitive molecules in polymeric materials through covalent[3−5] or noncovalent[6,7] modification facilitates color changes in response to macroscopic deformation. Alternatively, microencapsulation offers a robust and versatile platform where mechanical rupture triggers the release of a payload.[8,9] Enhanced damage visibility in polymer composites has been achieved using a fluorescent dye contained within embedded hollow fibers;[10] however, this method suffers from the absence of a "turn-on" mechanism, precluding its utility in transparent materials. Visualization of damage has also been accomplished using microcapsules containing a conjugated monomer in combination with an embedded polymerization catalyst[11] as well as pH-sensitive dyes that change color upon reaction with an auxiliary compound[12,13] or with certain functional groups present in the polymer matrix.[14] Chemical activation of an embedded fluorogenic molecule[15] and formation of a charge-transfer complex using a dual capsule

system has also been described.[16] Nevertheless, current damage detection methods generally rely on chemical reactions to elicit a response and are highly material-dependent or complicated by multiple components.

Here, we demonstrate a simple, robust, and sensitive fluorescence-based approach that employs a physical change of state to autonomously indicate damage in polymeric materials and composites by aggregation-induced emission (AIE). With this detection scheme, mechanical damage triggers rapid generation of a local fluorescence signal that is easily visualized under UV light and provides excellent contrast between intact and damaged regions of a material. The general indication mechanism enables the unaided detection of damage less than 2 μm in size in a wide variety of materials prepared using diverse fabrication methods.

Fluorescence detection provides significantly enhanced sensitivity over absorption-based colorimetric methods; however, typical fluorophores exhibit diminished emission with increasing concentration,[17] which restricts their use in materials applications. In contrast, AIE luminogens are molecules that possess vibrational and/or rotational modes capable of relaxing the energy of absorbed photons nonradiatively when dissolved in solution.[18,19] Aggregation restricts this intramolecular motion and promotes efficient photoluminescence.[20] This unique feature enables the use of AIE luminogens in areas such as solid state optoelectronic devices[21,22] and rewritable
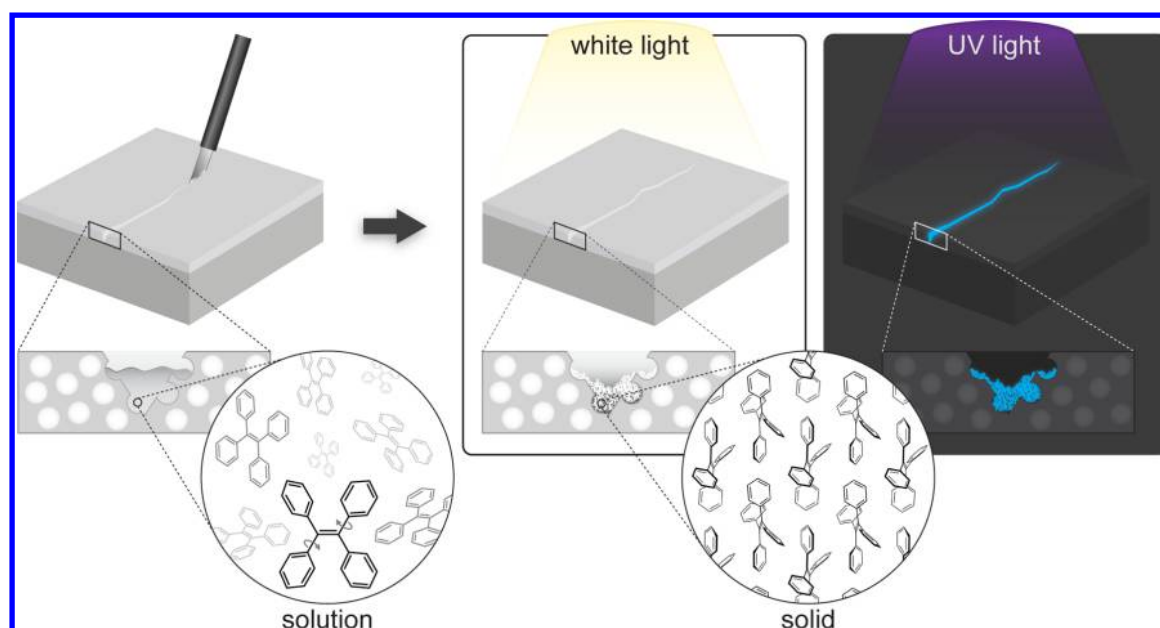
Figure 1. Schematic of the autonomous damage detection system. Core−shell microcapsules containing a dilute solution of AIE luminogen are embedded in a polymeric material. Mechanical damage causes microcapsules to rupture and release their liquid payload. Subsequent evaporation of the solvent causes solid AIE luminogen to deposit in the damaged region, which fluoresces under UV light. The core solutions contained within intact microcapsules remain nonemissive, providing excellent contrast between damaged and undamaged regions of the material.

media for optical data storage.[23,24] Building on these innovations, we envisioned a turn-on detection system in which core−shell microcapsules release a solution of an AIE luminogen upon mechanical damage resulting in local fluorescence indication after solvent evaporation.

The damage detection system is illustrated schematically in Figure 1. Core−shell microcapsules containing a dilute, nonfluorescent solution of AIE luminogen are embedded in a polymeric material. Following mechanical damage, rupture of the microcapsules results in the release of the encapsulated solution in the region of damage. Subsequent spontaneous evaporation of the solvent causes aggregation of the AIE luminogen and generation of fluorescence that is visualized under an appropriate excitation light source. This approach provides a number of advantages for damage detection. For example, this simple, one-component design does not rely on intermolecular interactions and is anticipated to perform similarly in a variety of materials. Furthermore, advancements in encapsulation chemistry, the ready availability of diverse AIE luminogens, and the facile incorporation of microcapsules into existing materials formulations make this technology highly accessible.

To demonstrate this concept, we investigated the commercially available AIE luminogen 1,1,2,2-tetraphenylethylene (TPE).[25,26] Hexyl acetate was chosen as a solvent due to its suitability for microcapsule preparation,[27] moderate boiling point (∼170 °C), and contemporary use in industrial paint formulations.[28] When TPE is dissolved in hexyl acetate, the solution is colorless and exhibits an absorption maximum at 310 nm (Figure 2a). As expected, the solution is nonemissive under illumination with UV light, but a brilliant blue fluorescence with an emission maximum at 450 nm is observed from the solid residue formed upon solvent evaporation (Figure 2b). The fluorescence excitation spectrum of solid TPE reveals relatively uniform emission intensity at excitation wavelengths between 300 and 370 nm, varying less than 10% over this range

(Figure S1). This expedient feature facilitates the use of ordinary UV light sources for visualization of the damage-induced fluorescence signal.

Core−shell microcapsules containing a 1 wt % (8.7 mg mL^{-1}, 26 mM) solution of TPE in hexyl acetate were prepared using a well-established *in situ* emulsification condensation polymerization method.[29] The TPE microcapsules studied were 112 ± 10 μm in diameter and exhibited excellent thermal stability up to 220 °C as demonstrated by thermogravimetric analysis (Figure S2). SEM images of the microcapsules show that the majority were spherical in shape and remained intact after processing (Figure S3). The thickness of the shell walls was approximately 300 nm based on analysis of SEM images of ruptured microcapsules. The TPE microcapsules are colorless due to the core material being completely transparent to all visible wavelengths of light, which is desirable for applications where the overall appearance of a material is potentially affected by the inclusion of additives. The fluorescence properties of TPE in solution were also maintained in the microcapsules, which were nonfluorescent under illumination with UV light, suggesting minimal background signal from the intact microcapsules when embedded in polymeric materials. The microcapsules remained nonemissive upon storage in ambient conditions for more than six months, which indicates the high stability of the TPE solutions contained in their core.

The potential for TPE microcapsules to enable visual indication of mechanical damage was first evaluated by optical microscopy of both intact and ruptured microcapsules under illumination with white light and UV light (Figure 2c). TPE microcapsules were spread on a glass substrate, and a portion of them was damaged using a razor blade. Under illumination with white light, regions where intact and ruptured microcapsules coexisted were clearly observed, facilitating investigation of the fluorescence properties of intact versus ruptured microcapsules at the single microcapsule level. Under illumination with UV light, microcapsules that were damaged (as observed under
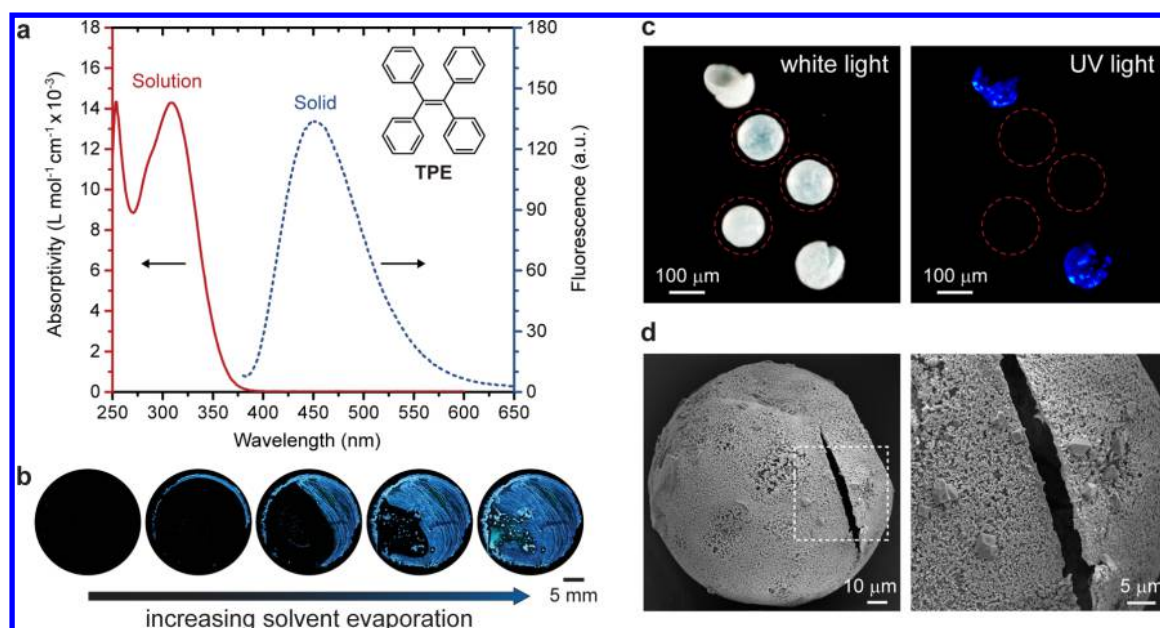
Figure 2. Characterization of TPE fluorescence. (a) UV−vis absorption (6.6×10^{-5} M in hexyl acetate) and solid-state fluorescence emission spectra of TPE (λ_{ex} = 365 nm). (b) Photographs of a TPE solution under illumination with UV light demonstrating the development of fluorescence upon solvent evaporation. (c) Stereomicrographs of TPE microcapsules under illumination with white light and UV light demonstrating damage-induced fluorescence. Intact microcapsules are undetectable under UV light, while ruptured microcapsules are fluorescent. The locations of intact microcapsules are outlined as a guide (red dashed circles). (d) SEM images of a ruptured TPE microcapsule showing formation of TPE crystals on the shell wall.

white light) exhibited distinct blue fluorescence while the intact microcapsules were undetectable. As a control, microcapsules containing only hexyl acetate in the core were also prepared and evaluated similarly. As expected, no fluorescence was detected from intact or ruptured control microcapsules, demonstrating that the TPE luminogen was responsible for the observed fluorescence response (Figure S4). Additionally, SEM images of ruptured TPE microcapsules revealed crystalline deposits on the surface of the capsule shell which were absent in images of the ruptured control microcapsules (Figure 2d).

Transparent epoxy coatings incorporating 10 wt % TPE microcapsules were prepared to investigate autonomous damage indication capabilities for self-reporting engineering thermoset materials. Cured films were scratched with a razor blade and evaluated under white light and UV light sources (Figure 3a). Photographs of the scratched coating highlight the significant enhancement in visual identification of the damaged area under exposure to UV light, while higher magnification stereomicrographs demonstrate localization of the fluorescence response to individually ruptured microcapsules. Critically, areas outside of the damaged region remained completely nonemissive, providing excellent contrast between the damaged and intact regions of the coating. Moreover, the fluorescence signal developed rapidly after mechanical damage and was detectable almost immediately under UV light. Time-dependent fluorescence microscopy measurements demonstrated that maximum fluorescence intensity was reached after approximately 5 min in ambient conditions (Figure 3b). Analogous coatings prepared with control microcapsules were evaluated in an identical fashion with no changes in fluorescence observed after damage (Figure S5).

Epoxy coatings containing TPE microcapsules also demonstrated persistent damage indication capabilities. Scratched coatings stored for over one month in ambient conditions

displayed equivalent fluorescence indication properties compared to freshly prepared and scratched coatings. Likewise, identical fluorescence behavior was observed for new scratches produced in aged coatings (Figure S6). Damage indication was also uncompromised using microcapsules with a lower concentration of TPE in the core and lower microcapsule loadings; however, higher TPE concentration and incorporation of more microcapsules in coatings produced a more intense fluorescence response, as expected (Figure S7).

Further studies were carried out to probe the relationship between fluorescence response and damage scale. SEM images of scratched epoxy coatings containing TPE microcapsules show solid deposits of TPE in sheared regions adjacent to the primary scratch damage (Figure 3c). Close inspection revealed evidence of ruptured microcapsules at the surface of the sheared region (Figure S8). The high number of exposed, ruptured microcapsules in this region likely results in accelerated solvent evaporation and accounts for the intense and relatively diffuse fluorescence around the primary damage site. Furthermore, we reasoned that this feature would manifest in a fluorescence signal that is closely correlated with damage size. A series of scratches with varying depths (ca. 94−376 μm) were created in a similar epoxy specimen, and the indication response was characterized using fluorescence microscopy (Figure 3d). The area of the fluorescent region and the average intensity increased proportionally with cutting depth. Analysis of the surface topology of the specimen using profilometry confirmed that the area of the fluorescence signal was strongly correlated with the physically damaged area which included significant shearing adjacent to the primary scratch (Figure 3e); however, profilometry was unable to fully resolve these damage features. The relationship between mechanical damage and fluorescence response was further confirmed by characterizing the internal structure of the specimen using X-ray computed microtomography (micro-CT), which was able to differentiate
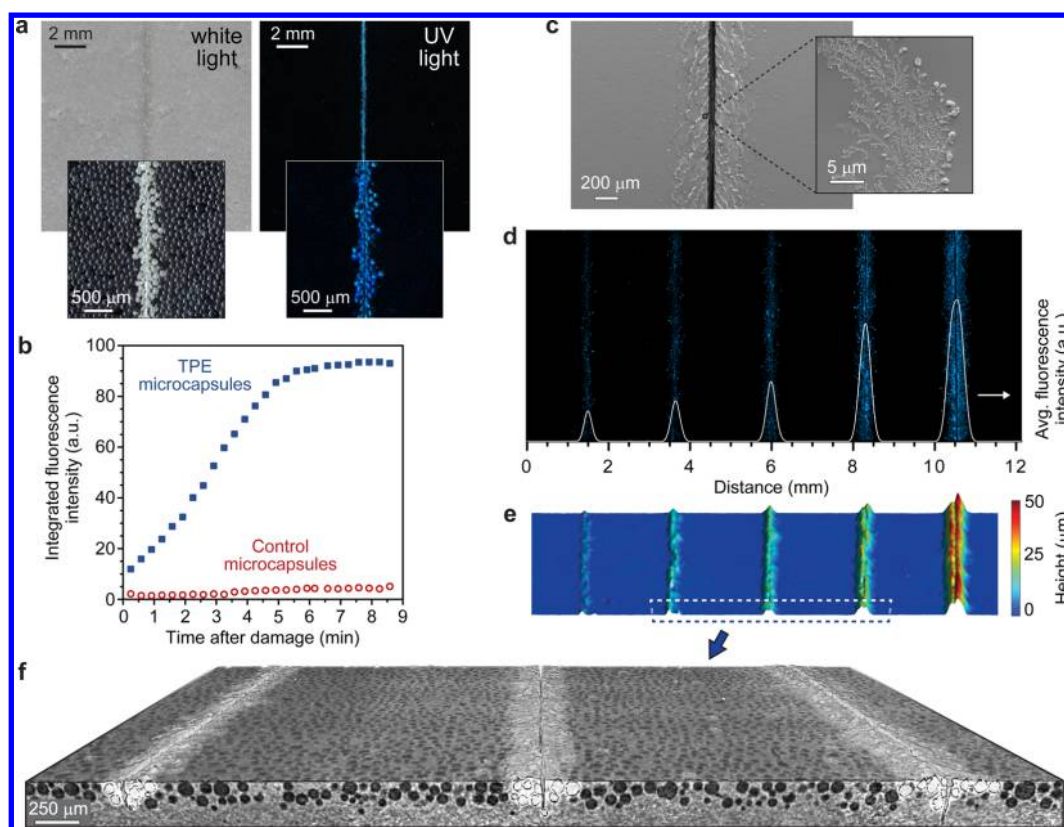
Figure 3. Evaluation of damage detection performance in transparent epoxy coatings. (a) Photographs of an epoxy coating containing 10 wt % TPE microcapsules under illumination with white light and UV light after being scratched with a razor blade. Insets show stereomicrographs of the coating under similar illumination. (b) Time-dependent fluorescence microscopy measurements illustrating rapid development of a fluorescence signal after damage. A control coating incorporating microcapsules with only hexyl acetate in the core exhibits negligible change in fluorescence after damage. (c) SEM images illustrating solid TPE deposits in the shear region adjacent to the primary scratch damage. (d−f) Characterization of an epoxy coating containing 10 wt % TPE microcapsules with damage of varying size (average scratch depths from left to right: 94, 140, 171, 222, and 376 μm): fluorescence micrograph and overlaid fluorescence intensity profile (d), surface topology from profilometry (e), and magnified view of a 3D micro-CT reconstruction (f). Profilometry does not sufficiently resolve the scratch from the adjacent sheared region. In panel f, intact microcapsules are rendered as black; ruptured microcapsules and damaged areas of the surface are white; the epoxy polymer matrix is shaded gray.

between intact and ruptured microcapsules within the material and identify their location relative to matrix damage (Figure 3f).

To demonstrate the versatility of this method, we also investigated damage detection performance in a variety of different materials and different damage modes. Polyurethane coatings incorporating 10 wt % TPE microcapsules were prepared and examined under white light and UV light after being scratched with a razor blade (Figure 4a). Under ambient white lighting, the damage to the coating was nearly undetectable; however, under illumination with a hand-held 365 nm UV lamp, the scratch was clearly visible, exhibiting a bright blue fluorescence signal. Similar to the epoxy coatings, intense fluorescence from the region of damage was detected rapidly after the coating was scratched. SEM analysis revealed that the scratch was <2 μm wide, which is beyond the putative limit of unaided visual detection. Similar damage to coatings containing control microcapsules was undetectable (Figure S9). Scratch damage was also clearly indicated in a variety of other polymeric coatings prepared using diverse fabrication techniques (Figure 4b). TPE microcapsules provided excellent detection performance in polydimethylsiloxane, UV-cured epoxy, poly(acrylic acid) cast from water, and polystyrene cast from toluene. The effectiveness of damage indication in these materials also highlights advantages of this approach over

color changing strategies, which are typically limited to polymer matrices with minimal coloration to provide sufficient contrast. Additionally, performance is maintained in materials utilizing diverse chemistries and curing conditions including prolonged exposure to intense UV irradiation. Finally, the ability to enhance damage visibility in carbon fiber reinforced composites was investigated, where barely visible impact damage is accompanied by severe deterioration in structural integrity.[30] Composite specimens with an epoxy coating incorporating 10 wt % TPE microcapsules were subjected to a variety of impact tests, and the resulting damage, including microcracks, was clearly discernible under UV light (Figure 4c and Figure S10). These experiments further illustrate the versatility of this technology and highlight the unique efficacy of this self-reporting system for enhancing the visual identification of damage in different materials systems.

Self-reporting materials with autonomous damage indication are achieved using core−shell microcapsules containing a dilute solution of an AIE luminogen. This system constitutes a simple and robust method that enables the visual detection of microscopic damage in a wide range of polymeric materials under illumination with an appropriate excitation light source. Using microcapsules containing a solution of TPE in hexyl acetate, the fluorescence signal develops rapidly following mechanical damage to polymeric coatings and reaches
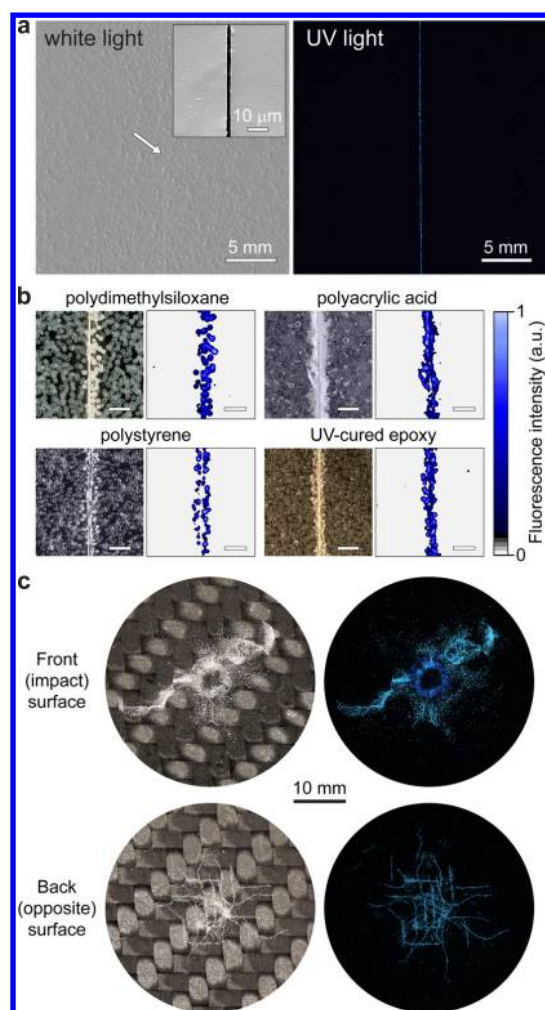
Figure 4. Damage detection in a variety of materials and different damage modes. (a) Photographs of polyurethane coatings containing 10 wt % TPE microcapsules under illumination with white light and UV light after being scratched with a razor blade. Inset shows an SEM image of the scratch. (b) Stereomicrographs and corresponding fluorescence intensity maps of a variety of coating materials containing 10 wt % TPE microcapsules after being scratched with a razor blade (scale bars, 500 μm). (c) Photographs under white light and UV light of carbon fiber reinforced composite panels with an epoxy coating containing 10 wt % TPE microcapsules after impact.

maximum intensity in minutes. In contrast to alternative methods, this detection system is general, does not rely on any external or intermolecular interactions to elicit a response, and provides outstanding contrast between intact and damaged regions with excellent sensitivity. We anticipate that the effectiveness of this technology coupled with its facile implementation will make it a useful tool for a variety of applications extending beyond damage detection.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.6b00198.

> Materials and experimental methods, preparation of microcapsules and coatings, image analysis, and additional characterization data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: jsmoore@illinois.edu.
*E-mail: n-sottos@illinios.edu.

Author Contributions
§M.J.R. and W.L. contributed equally.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Kessler, S. S.; Spearing, S. M.; Soutis, C. Damage Detection in Composite Materials Using Lamb Wave Methods. *Smart Mater. Struct.* **2002**, *11*, 269.

(2) Bruns, N.; Pustelny, K.; Bergeron, L. M.; Whitehead, T. A.; Clark, D. S. Mechanical Nanosensor Based on FRET within a Thermosome: Damage-Reporting Polymeric Materials. *Angew. Chem., Int. Ed.* **2009**, *48*, 5666–5669.

(3) Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martínez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. Force-Induced Activation of Covalent Bonds in Mechanoresponsive Polymeric Materials. *Nature* **2009**, *459*, 68–72.

(4) Chen, Y.; Spiering, A. J. H.; Karthikeyan, S.; Peters, G. W. M.; Meijer, E. W.; Sijbesma, R. P. Mechanically Induced Chemiluminescence from Polymers Incorporating a 1,2-Dioxetane Unit in the Main Chain. *Nat. Chem.* **2012**, *4*, 559–562.

(5) Imato, K.; Irie, A.; Kosuge, T.; Ohishi, T.; Nishihara, M.; Takahara, A.; Otsuka, H. Mechanophores with a Reversible Radical System and Freezing-Induced Mechanochemistry in Polymer Solutions and Gels. *Angew. Chem., Int. Ed.* **2015**, *54*, 6168–6172.

(6) Löwe, C.; Weder, C. Oligo(p-Phenylene Vinylene) Excimers as Molecular Probes: Deformation-Induced Color Changes in Photoluminescent Polymer Blends. *Adv. Mater.* **2002**, *14*, 1625–1629.

(7) Donati, F.; Pucci, A.; Cappelli, C.; Mennucci, B.; Ruggeri, G. Modulation of the Optical Response of Polyethylene Films Containing Luminescent Perylene Chromophores. *J. Phys. Chem. B* **2008**, *112*, 3668–3679.

(8) White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. Autonomic Healing of Polymer Composites. *Nature* **2001**, *409*, 794–797.

(9) Blaiszik, B. J.; Kramer, S. L. B.; Olugebefola, S. C.; Moore, J. S.; Sottos, N. R.; White, S. R. Self-Healing Polymers and Composites. *Annu. Rev. Mater. Res.* **2010**, *40*, 179–211.

(10) Pang, J. W. C.; Bond, I. P. Bleeding Composites—damage Detection and Self-Repair Using a Biomimetic Approach. *Composites, Part A* **2005**, *36*, 183–188.

(11) Odom, S. A.; Jackson, A. C.; Prokup, A. M.; Chayanupatkul, S.; Sottos, N. R.; White, S. R.; Moore, J. S. Visual Indication of Mechanical Damage Using Core—Shell Microcapsules. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4547–4551.

(12) Vidinejevs, S.; Aniskevich, A. N.; Gregor, A.; Sjöberg, M.; Alvarez, G. Smart Polymeric Coatings for Damage Visualization in Substrate Materials. *J. Intell. Mater. Syst. Struct.* **2012**, *23*, 1371–1377.

(13) Vidinejevs, S.; Strekalova, O.; Aniskevich, A.; Gaidukov, S. Development of a Composite with an Inherent Function of Visualization of a Mechanical Action. *Mech. Compos. Mater.* **2013**, *49*, 77−84.

(14) Li, W.; Matthews, C. C.; Yang, K.; Odarczenko, M. T.; White, S. R.; Sottos, N. R. Autonomous Indication of Mechanical Damage in Polymeric Coatings. *Adv. Mater.* **2016**, *28*, 2189−2194.

(15) van den Dungen, E. T. A.; Loos, B.; Klumperman, B. Use of a Profluorophore for Visualization of the Rupture of Capsules in Self-Healing Coatings. *Macromol. Rapid Commun.* **2010**, *31*, 625−628.

(16) Lavrenova, A.; Farkas, J.; Weder, C.; Simon, Y. C. Visualization of Polymer Deformation Using Microcapsules Filled with Charge-Transfer Complex Precursors. *ACS Appl. Mater. Interfaces* **2015**, *7*, 21828−21834.

(17) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970.

(18) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. Aggregation-Induced Emission of 1-Methyl-1,2,3,4,5-Pentaphenylsilole. *Chem. Commun.* **2001**, 1740−1741.

(19) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission: Phenomenon, Mechanism and Applications. *Chem. Commun.* **2009**, 4332−4353.

(20) Mei, J.; Hong, Y.; Lam, J. W. Y.; Qin, A.; Tang, Y.; Tang, B. Z. Aggregation-Induced Emission: The Whole Is More Brilliant than the Parts. *Adv. Mater.* **2014**, *26*, 5429−5479.

(21) Zhao, Z.; Chan, C. Y. K.; Chen, S.; Deng, C.; Lam, J. W. Y.; Jim, C. K. W.; Hong, Y.; Lu, P.; Chang, Z.; Chen, X.; Lu, P.; Kwok, H. S.; Qiu, H.; Tang, B. Z. Using Tetraphenylethene and Carbazole to Create Efficient Luminophores with Aggregation-Induced Emission, High Thermal Stability, and Good Hole-Transporting Property. *J. Mater. Chem.* **2012**, *22*, 4527−4534.

(22) Banal, J. L.; White, J. M.; Lam, T. W.; Blakers, A. W.; Ghiggino, K. P.; Wong, W. W. H. A Transparent Planar Concentrator Using Aggregates of Gem-Pyrene Ethenes. *Adv. Energy Mater.* **2015**, *5*, 1500818.

(23) Zhang, G.; Lu, J.; Sabat, M.; Fraser, C. L. Polymorphism and Reversible Mechanochromic Luminescence for Solid-State Difluoroboron Avobenzone. *J. Am. Chem. Soc.* **2010**, *132*, 2160−2162.

(24) Wang, J.; Mei, J.; Hu, R.; Sun, J. Z.; Qin, A.; Tang, B. Z. Click Synthesis, Aggregation-Induced Emission, E/Z Isomerization, Self-Organization, and Multiple Chromisms of Pure Stereoisomers of a Tetraphenylethene-Cored Luminogen. *J. Am. Chem. Soc.* **2012**, *134*, 9956−9966.

(25) Dong, Y.; Lam, J. W. Y.; Qin, A.; Liu, J.; Li, Z.; Tang, B. Z.; Sun, J.; Kwok, H. S. Aggregation-Induced Emissions of Tetraphenylethene Derivatives and Their Utilities as Chemical Vapor Sensors and in Organic Light-Emitting Diodes. *Appl. Phys. Lett.* **2007**, *91*, 011111.

(26) Zhao, Z.; Lam, J. W. Y.; Tang, B. Z. Tetraphenylethene: A Versatile AIE Building Block for the Construction of Efficient Luminescent Materials for Organic Light-Emitting Diodes. *J. Mater. Chem.* **2012**, *22*, 23726−23740.

(27) Caruso, M. M.; Blaiszik, B. J.; White, S. R.; Sottos, N. R.; Moore, J. S. Full Recovery of Fracture Toughness Using a Nontoxic Solvent-Based Self-Healing System. *Adv. Funct. Mater.* **2008**, *18*, 1898−1904.

(28) Stoye, D. Solvents. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2000; Vol. 33, pp 619−688.

(29) Caruso, M. M.; Blaiszik, B. J.; Jin, H.; Schelkopf, S. R.; Stradley, D. S.; Sottos, N. R.; White, S. R.; Moore, J. S. Robust, Double-Walled Microcapsules for Self-Healing Polymeric Materials. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1195−1199.

(30) Richardson, M. O. W.; Wisheart, M. J. Review of Low-Velocity Impact Properties of Composite Materials. *Composites, Part A* **1996**, *27*, 1123−1131.